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U.V. Photoelectron (He I and He II) Studies of $M(CO)_5PX_3$ (M = Cr, Mo, W and X = F, Cl, Br)

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The He I and He II spectra of the complexes $M(CO)_5PX_3$ (M = Cr, Mo, W; X = F, Cl, Br) are presented. The assignment was based on the comparison with the spectra of the separate PX_3 and $M(CO)_6$ molecules concerning the positions of the bands and the intensity differences in going from He I to He II. Conclusions about the σ- and π-bonding in the complexes and about charge on the metals could be drawn. Correlations between the ionization potentials and infrared frequencies could be demonstrated.

Introduction

The valence region photoelectron spectra of the group VIb hexacarbonyls and of a small number of monosubstituted species have been reported [1–4]. Besides these complexes have also been the subject of several M.O. calculations [2, 4–6].

Contrary to N-donor ligands, P-donor ligands possess an empty 3d-orbital on the phosphorus atom. The importance of this orbital in the complexes has been discussed with use of several techniques [7–9]. The photoelectron spectra of the free phosphorus trihalide ligands have been well established [10, 11]. Calculations of PF_3 [12, 13] and PCl_3 [13, 14] have been published confirming the proposed assignment.

The assignments of the spectra under study could be based on a comparison with known spectra. In addition to the position of the bands the intensities and especially intensity-differences of bands between He I and He II spectra will give us information about the assignments. These He I/He II intensity ratios show regular patterns in the series. The theory and the calculation of intensity ratios in view of the He I and He II-photons have been published before [15].

Experimental

Preparations

All reactions were carried out under dry deoxygenated nitrogen. PF_3, PCl_3, PBr_3 and the metal hexacarbonyls were analytically pure and used without purification.

The $M(CO)_5PF_3$ compounds were made by adding PF_3 to the tetrahydrofuran complexes [16] until its partial pressure was 200 torr. After 12 hours of shaking the solvent was removed under vacuum and the compound was purified [17, 18]. $M(CO)_5L$ (L = PCl_3, PBr_3) were also made from their corresponding tetrahydrofuran complexes, except for $Mo(CO)_5PCl_3$ and $Mo(CO)_5PBr_3$. $Mo(CO)_5PCl_3$ was made in refluxing $Mo(CO)_6$ and an excess of PCl_3 in methylcyclohexane [19, 20]. The PBr_3 derivative was made from the methylmethoxycarbene complex using the method described by Fischer [21]. All the compounds were characterized by infrared spectroscopy and elemental analyses.

Physical Measurement

The photoelectron spectra were recorded on a Perkin–Elmer P.S. 18 spectrometer modified with a Helectros He I/He II source. All samples were very volatile and could be run at room temperature. A volatile sample inlet system was used. The temperature of the ionization chamber was maintained as low as possible (~40 °C). Partial decomposition of $Mo(CO)_5PBr_3$ could however not be avoided. The spectra were calibrated by various mixtures of methyl iodide, xenon, argon and oxygen [22] before and after running the spectra in order to ascertain that no drift had taken place. The band areas were measured by a Hewlett Packard digitizer system model 64 controlled by a calculator model 10.

Results

Free Phosphorus Trihalide Ligands

The PX_3 ligands are assumed to possess local C_{3v} symmetry in the complexes although the apical angle may differ in the free ligands. The highest occupied molecular orbital is mainly the phosphorus lone pair (a_1). Chemical intuition confirms the trend to higher energy going from fluorine to bromine. The next four orbitals have symmetry e (twice), a_2 and a_1

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TABLE I. Vertical Ionization Potentials (eV) Relative Intensities and Assignment of the Free PX_3 (X = F, Cl, Br).

PF_3				PCl_3				PBr_3			
i.p.	$I_{He\ I}$	$I_{He\ II}$		i.p.	$I_{He\ I}$	$I_{He\ II}$		i.p.	$I_{He\ I}$	$I_{He\ II}$	
12.28	1.0	1.0	a_1	10.54	1.0	1.0	a_1	9.99	1.0	1.0	a_1
15.89	4.8	7.3	e	11.71	1.4	0.6	a_2	10.59	2.6	2.1	e
16.29			a_2	12.01	3.5	1.5	e	10.80			
17.35	5.0	3.0	e	12.96	3.5	1.5	e	11.11	1.7	1.5	a_2
18.51	2.6	1.1	a_1	14.25	1.4	0.8	a_1	11.78	3.1	2.5	e
19.31	8.2	3.6	e	15.22	2.2	1.4	e	13.07	1.0	0.8	a_1
22.4		1.4	a_1	18.86		0.5	a_1	14.04	1.7	1.6	e
											a_1

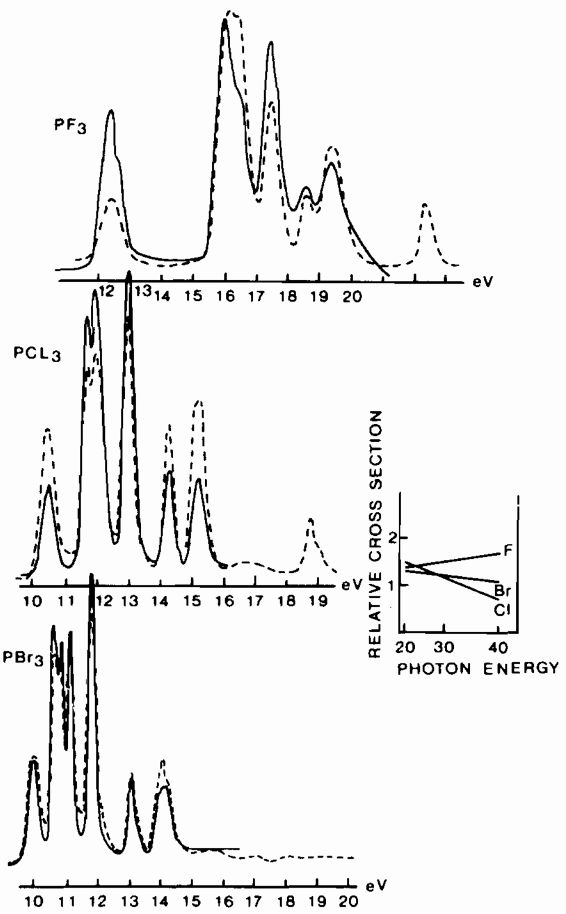

Figure 1. The He I (———) and He II (--------) photoelectron spectra of free PX_3 (X = F, Cl, Br). In the diagram on the right the average cross section of the halogen p-orbital relative to the band of the phosphorus lone pair is drawn against the photon energy.

respectively, and are composed of the six halogen p-orbitals perpendicular to the P–X axis. The orbitals of a_1- and e-symmetry will interact with the appropriate 3d-orbitals of phosphorus giving rise to the P–X π-bonding. The three σ P–X bonds are of a_1- and e-symmetry. Spin orbit coupling may lift the degeneracy as is demonstrated in the spectra of PBr_3.

The ionization potentials and the assignments are given in Table I and in Figure 1 together with their intensity behaviour in going from He I to He II. The intensities are taken relative to the lone pair of the phosphorus atom. Corrections of the peak areas were made as described in reference 15.

Figure 1 reveals that the fluorine lone pair intensity remains essentially unchanged whereas the chlorine and bromine lone pair intensity decreases with respect to lone pair P, the chlorine intensity more than the bromine one.

$M(CO)_6$

The hexacarbonyl u.v. photoelectron spectra are well known [1]. The first band belongs to the t_{2g} m.o. with predominantly metal d-character. The intensity increases from He I to He II relative to the 5σ and 1π carbonyl orbitals. This band may split due to spin–orbit coupling as is the case in $W(CO)_6$.

The next seven bands (13.4–16.2 eV) are derived from the CO 1π and 5σ-orbitals. The two bands at 17.8 eV and 19.7 eV originate from the 4σ-ligand orbital.

$M(CO)_5L$

The He I and He II spectra of the complexes are shown in the Figures 2–6. In order to facilitate a direct comparison the spectra of the phosphorus trihalides are added in figure 4, 5 and 6. The measured vertical ionization potentials are listed in Table II together with the proposed assignment. The corrected intensities of some bands expressed as their respective peak areas relative to the peak area of the metal d-orbital band are summarized in Table III.

In the treatment of the spectra of the complexes the following separation into three types of orbitals will be made:

a) predominantly metal d-orbitals

b) orbitals originating mainly from phosphorus trihalide

c) orbitals chiefly localised on the carbonyl ligands.

TABLE II. Vertical Ionization Potentials (eV) and Assignment of M(CO)$_5$PX$_3$ (M = Cr, Mo, W and X = F, Cl, Br).

	Metal d-orbitals	σ M–P			5σ, 1πCO			e + a_2 l.p.	4σCO c l.p.	l.p. + eσ	a_1 σ
Cr(CO)$_5$PF$_3$	8.56	12.48			13.64	14.26		15.7	17.8	19.4	22.43
Mo(CO)$_5$PF$_3$	8.55										
W(CO)$_5$PF$_3$	8.68	12.48			13.65	14.90		15.7	17.7	19.3	22.35
	Metal d-orbitals	σ M–P	a_2 l.p. e.l.p.	e.l.p.	5σ, 1πCO				4σCO		
Cr(CO)$_5$PCl$_3$	8.32	11.08	11.76	12.83	13.40	14.24	15.23		17.8	19.2	23.4
Mo(CO)$_5$PCl$_3$	8.36	10.96	11.66	12.75	13.15	14.40	15.07		17.6	19.4	23.5
W(CO)$_5$PCl$_3$	8.39	10.99	11.61	12.70	13.11	14.69			17.6	19.9	23.3
	Metal d-orbitals	σ M–P e l.p.	a_2 l.p.	e l.p.	5σ, 1πCO a_1 l.p.				4σCO		
Cr(CO)$_5$PBr$_3$	8.32	10.51	10.97	11.72	13.29	14.04			17.6	19.7	22.8
Mo(CO)$_5$PBr$_3$	8.33										

TABLE III. Vertical Ionization Potentials (eV) and Relative Intensities of M(CO)$_5$PX$_3$ (M = Cr, Mo, W and X = F, Cl, Br).

Cr(CO)$_5$PF$_3$	i.p.	8.56	12.48		
	I(He I)	1.0	0.73		
	I(He II)	1.0	0.41		
W(CO)$_5$PF$_3$	i.p.	8.68	12.48		
	I(He I)	1.0	0.46		
	I(He II)	1.0	0.33		
Cr(CO)$_5$PCl$_3$	i.p.	8.32	11.08	11.76	
	I(He I)	1.0	0.90	4.7	
	I(He II)	1.0	0.14	0.34	
Mo(CO)$_5$PCl$_3$	i.p.	8.36	10.95	11.66	
	I(He I)	1.0	0.61	2.9	
	I(He II)	1.0	0.11	0.22	
W(CO)$_5$PCl$_3$	i.p.	8.39	10.99	11.61	
	I(He I)	1.0	0.75	3.4	
	I(He II)	1.0	0.09	0.22	
Cr(CO)$_5$PBr$_3$	i.p.	8.32	10.51	10.97	11.72
	I(He I)	1.0	3.9	1.6	3.3
	I(He II)	1.0	0.97[a]		0.59

[a] The lower resolution of the He II spectrum made a deconvolution like in He I impossible.

The Metal d-Orbitals

The first band in the photoelectron spectra of the complexes is assigned to the metal d-orbitals. The position agrees with those of the hexacarbonyls, while the shape is quite similar. In W(CO)$_5$PX$_3$ (X = F, Cl) a shoulder at the high energy side was observed just as in W(CO)$_6$ [1] (see Figure 4). The splitting is much smaller in the pentacarbonyls and a spin–orbit coupling constant of 0.14 eV for both complexes was determined [23]. However, this value could not be determined with high accuracy due to the low resolution of the spectra.

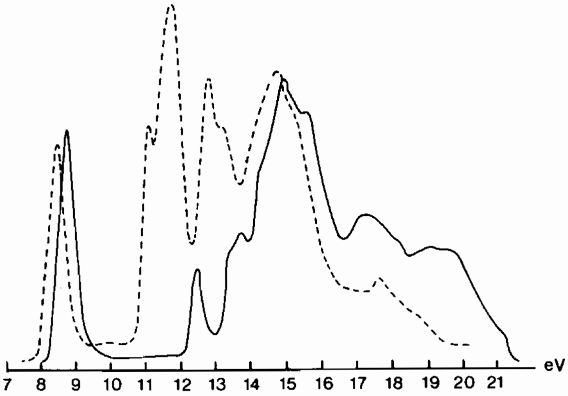

Figure 2. The He I photoelectron spectra of W(CO)$_5$PF$_3$ (———) and W(CO)$_5$PCl$_3$ (-------).

Phosphorus Trihalide Orbitals

M(CO)$_5$PF$_3$ (M = Cr, W)

In the M(CO)$_5$PF$_3$ complexes (M = Cr, W) the position of the metal–phosphorus orbital is the next highest ionization potential in the spectra. The bands are not obscured by other bands.

The bands belonging to the lower lying fluorine lone pair orbitals, however, are obscured by those of the σ- and π-orbital combinations of the five carbon monoxide ligands. Nevertheless the positions of these bands could be estimated by assuming that the photoelectron bands originating from the M(CO)$_5$ moiety are similar in all the complexes. For instance the He I spectrum in Figure 2 from 14 eV upwards shows

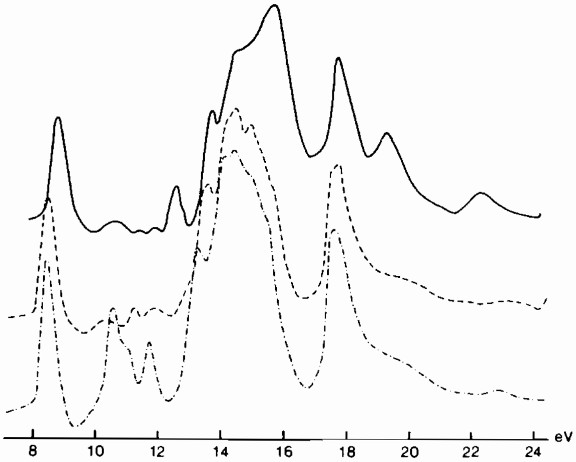

Figure 3. The He II photoelectron spectra of $Cr(CO)_5PF_3$ (———), $Cr(CO)_5PCl_3$ (-------) and $Cr(CO)_5PBr_3$ (·······).

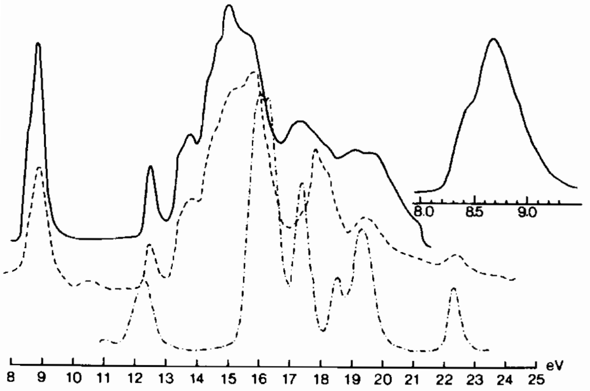

Figure 4. The He I (———) and He II (-------) photoelectron spectrum of $W(CO)_5PF_3$ and the He II (·······) spectrum of PF_3. Right above, d-orbital on expanded scale.

some of the bands from the PF_3 moiety in good agreement with the free ligand values. An even better picture is shown in Figure 3, since in that case the effect of the analyser discrimination is almost vanished.

So four bands originating from the PF_3 part could be found at 15.7 eV, 17.8 eV, 19.4 eV and 22.4 eV. The 17.8 eV band must also be described as partly from PF_3, since this broad band is of higher intensity than in the corresponding PCl_3 and PBr_3 complexes. Based on the assignment of the free PF_3 ligand and in comparison with the He I spectra of $M(PF_3)_6$ (M = Cr, Mo, W) [24] and $M(PF_3)_4$ (M = Ni, Pd, Pt) [25] we made the following tentative assignment (see also Figure 4):

Cr	W	
15.7	15.7	($e + a_2$; l.p. F)
17.8	17.7	(e; l.p. F)
19.4	19.3	(a_1; l.p. F + e; σPF)
22.43	22.35	(a_1; σPF)

$M(CO)_5PCl_3$ (M = Cr, Mo, W)

The positions of the orbitals mainly PCl_3 in character are established in Figure 2. The additional bands and the higher intensity of the $M(CO)_5PCl_3$ spectrum in the region from 11.0 to 15.0 eV is attributed to PCl_3 orbitals.

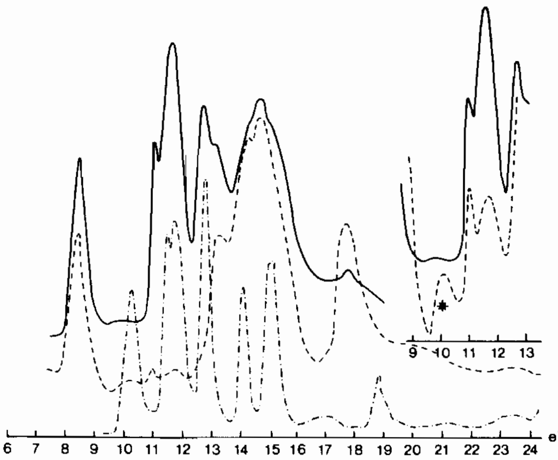

Figure 5. The He I (———) and He II (-------) photoelectron spectrum of $W(CO)_5PCl_3$ and the He II (·······) spectrum of PCl_3. Right above He I on lower count range and He II of $W(CO)_5PCl_3$. * is the 4σ-level of CO due to He II(β) emission (256 Å).

Examination of the known and measured values showed that an almost linear relationship exists between the ionization potential of the d-orbitals in the complexes $Cr(CO)_5PX_3$ ($X = CH_3$ [2], H [2], F) and the stabilization of the lone pair phosphorus orbital upon complexation. From this relationship and the ionization potential of the metal d-orbital in $Cr(CO)_5PCl_3$ the stabilization energy of the phosphorus lone pair of PCl_3 upon complexation was estimated as 0.5 eV. In this way the band at 11.0 eV is assigned to the σ M–P orbital.

Based on the assignment for the free PCl_3 molecule made by Potts *et al.* [10] we assume that the a_2- and e-lone pairs of Cl (at 11.7 and 12.01 eV respectively) merge into one broad band at about 11.7 eV. The e-lone pair of Cl at 12.96 eV is slightly destabilized upon complexation and attributed to the sharp band at 12.8 eV.

The shoulder at the low energy-side of this band is a carbonyl orbital. It is noted that in general the carbonyl bands do not alter so much in intensity by switching from He I to He II.

The positions of the PCl_3 bands with higher ionization potentials, that is, 14.25 eV (a_1; l.p. Cl), 15.22 eV (e; σP–Cl) and 18.86 eV (a_1; σP–Cl) are completely obscured by carbonyl bands.

The relative band intensities in the He I and He II are tabulated in Table IV and shown in Figure 5. In view of the possible errors made by the deconvolution, the behaviour of the intensities confirm the proposed assignment very well. The substantial decrease in intensity of the chlorine lone pairs in comparison with the phosphorus lone pair is again characteristic.

TABLE IV. Band Intensities Relative to Lone Pair P or σM–P of the He I and He II Photoelectron Spectra of M-$(CO)_5PCl_3$ (M = Cr, Mo, W) and Free PCl_3.

He I	σ M–P (a_1)	Lone Pair Cl(e + a_2)	Lone Pair Cl(e)
PCl_3	1.0	4.0	2.4
$Cr(CO)_5PCl_3$	1.0	4.7	2.5
$Mo(CO)_5PCl_3$	1.0	4.3	2.3
$W(CO)_5PCl_3$	1.0	4.8	a
He II			
PCl_3	1.0	2.0	1.3
$Cr(CO)_5PCl_3$	1.0	2.4	a
$Mo(CO)_5PCl_3$	1.0	1.9	a
$W(CO)_5PCl_3$	1.0	2.1	a

[a] Bands too much obscured to determine relative intensity.

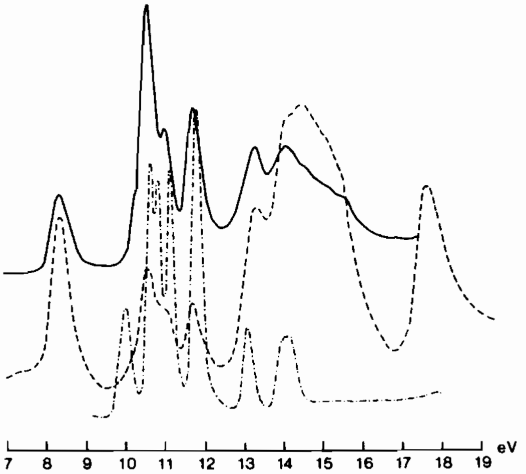

Figure 6. The He I (———) and He II (--------) photoelectron spectrum of $Cr(CO)_5PBr_3$ and the He I (·······) spectrum of PBr_3.

$M(CO)_5PBr_3$ (M = Cr, Mo)

As the ionization potential of the metal d-orbitals in $M(CO)_5PCl_3$ and $M(CO)_5PBr_3$ (M = Cr, Mo) is almost the same and the ionization potential of the phosphorus lone pair is only slightly lower in PBr_3 than in PCl_3, a similar shift of 0.5 eV for the phosphorus lone pair is expected upon complexation. That is why the intense band at 10.5 eV is partly assigned to the σ M–P orbital.

The assignment of the other PBr_3 orbitals is both established by comparison with the photoelectron spectra of $M(CO)_5PF_3$ (see Figure 3), PBr_3 (see Figure 6) and by relative intensity measurements of He I and He II spectra. Also here only small shifts of the bromine lone pair orbitals to lower binding energy are noticed. The two bands at 10.59 eV and 10.80 eV in free PBr_3, assigned to the e-orbital combination and split by spin–orbit coupling in the ionic state, merge and coincide with the M–P orbital at 10.51 eV in the Cr complex. Also the a_2 lone pair Br and e lone pair Br respectively at 11.11 and 11.78 eV slightly destabilize upon complexation. Their ionization potentials are 10.97 and 11.72 eV.

The band at 13.29 eV in the Cr complex probably belongs to both a carbonyl and a PBr_3 orbital. Its position agrees quite well with the ionization potential of the highest occupied orbital of the carbonyl group, *e.g.* $Cr(CO)_5PF_3$, while its high intensity in He I and strong decrease in the He II spectrum indicate the additional presence of a PBr_3 orbital. The a_1 lone pair bromine orbital at 13.07 eV seems obvious.

The remaining e and a_1 σP–Br orbitals are too much obscured by carbonyl bands and could not be localized.

The changes in the relative intensities of the PBr_3 bands are small in going from He I to He II. The intensities of the bands in the complexes and in the free ligands are quite similar as is shown in Table V.

Carbonyl Orbitals

Just as has been found for other $M(CO)_5L$ complexes [2, 3, 26] the broad band between 13 and 17 eV is primarily due to ionizations that can be related to the carbonmonoxide 5 σ(14.01 eV) and 1 π(16.53 eV) levels. Features to higher ionization potentials

TABLE V. Relative Band Intensities of PBr_3 Orbitals in the He I and He II Photoelectron Spectra of the Free Ligand and Cr-$(CO)_5PBr_3$ Complex.

He I	σ M–P (a_1) and Lone Pair Br(e)	Lone Pair Br(a_2)	Lone Pair Br(e)
PBr_3	2.4	1.0	1.7
$Cr(CO)_5PBr_3$	2.7	1.0	1.9
He II	σ M–P (a_1) and Lone Pair Br(e + a_2)[a]		Lone Pair Br(e)
PBr_3	1.9		1.0
$Cr(CO)_5PBr_3$	1.7		1.0

[a] The lower resolution of the He II spectrum made a deconvolution like in He I impossible.

are derived from the ligand 4 σ(19.68 eV) level. Apart from additional phosphorus trihalide bands, especially in $M(CO)_5PF_3$, the region above 17.0 eV is very similar to the hexacarbonyls. The intensive band at ~17.7 eV is in analogy to the hexacarbonyls attributed to the a_1, b_1 and e molecular orbitals, while the shoulder at higher ionization potential is assigned a_1 correlated with the a_{1g} in O_h-symmetry.

Finally we report a very weak band in the region 22.0 to 24.0 eV. The band is obscured in $M(CO)_5PF_3$ by the a_1 σ P–F orbital, but is probably also present there. It has also been observed for the hexacarbonyls [1].

Discussion

Bonding

Upon coordination of a phosphorus trihalide a similar bonding mechanism as for carbonyls is accepted [30]. The lone pair of the sp^3-hybridised phosphorus atom will form the metal–ligand σ-bond, while the low lying empty d-orbitals are capable of π-backbonding.

The position of the metal t_{2g}-orbitals (in local O_h symmetry) within a series of $M(CO)_5L$ complexes is at a first look only dependent on the amount of π-backbonding. Looking closer, this position is also dependent on the charge on the metal atom, hence on both the σ-donation and π-backbonding.

In $M(CO)_5PF_3$ the stabilization of the first band amounts about 0.1 to 0.2 eV with respect to the hexacarbonyls. It is in general accepted that PF_3 is a better π-acceptor than CO [17, 31, 32]. We can only conclude, however, from the photoelectron spectra that PF_3 is a better electron withdrawing ligand than CO [33]. This is confirmed by the ionization potentials of the d-orbitals of $M(PF_3)_6$ [24]. Within the series $M(CO)_6$, $M(CO)_5PF_3$ until $M(PF_3)_6$ even a linear relationship between the ionization potentials of these d-orbitals and the number of substituents seems to hold. When fluorine is replaced by the less electronegative chlorine and bromine the π-backbonding is clearly reduced relative to the σ-donation as is reflected by the lower first ionization potentials of the latter complexes. The difference, however, between PCl_3 and PBr_3 is not of much importance.

Although there is a local C_{4v} symmetry about the central metal atom, no splitting of the t_{2g}-orbital in e and b_2 could be observed for $M(CO)_5PX_3$, where X = F, Cl, Br, contrary to those complexes where X = H, CH_3. So for strong electronegative groups an electronic local O_h symmetry for the occupied orbitals maintains.

The low value for the spin–orbit coupling constant of $W(CO)_5PX_3$ (0.14) in comparison to the constants of $W(CO)_6$ (0.17) and $W(CO)_5L$ (L = nitrogen donor ligand) (0.23–0.31) [1–3] can be interpreted in terms of a higher delocalisation of the d-electron in $W(CO)_5PX_3$ and stresses the importance of the phosphorus d_π-orbital.

The stabilization of the phosphorus lone pair will reflect the σ-donation of the ligand. The measured value for this stabilization in $M(CO)_5PF_3$ (0.2 eV) is much smaller than in $Cr(CO)_5PH_3$ (0.85 eV) and $Cr(CO)_5P(CH_3)_3$ (1.35 eV), stressing the insignificance of the σ-donation in the PF_3 complex.

A trend is found between this stabilization of the lone pair phosphorus and the amount of σ-donation on one hand and both the values for the ionization potentials of this lone pair in the free ligand and the sp-character of this lone pair as calculated from *ab initio* SCF-MO for a series of PX_3 molecules (X = F, H, CH_3) [12] on the other hand. The comparison between the amounts of stabilization of the lone pair on complexation in N-donor and those in P-donor complexes is remarkable. Within both series the mentioned relationship between i.p. of the free ligand and this stabilization energy holds. This stabilization energy in the N-donor complexes, however, is about twice as large as in the P-donor complexes. Apart from the energy of the lone pair orbital forming the metal–ligand σ-bond, clearly overlap of the metal and ligand orbitals does play an important role.

As it is assumed that the lone pair of the halogens reflects the net result of σ-donation and π-backbonding between the metal and the ligand [34], it is concluded that within the series $M(CO)_5PCl_3$ the transfer of negative charge from the ligand to the metal decreases in the order Cr > Mo > W. Within the series of complexes the σ-donation of the W complex, estimated from the stabilization energy of the phosphorus lone pair upon complexation, turned out to be too high. So an extra amount of π-backbonding must be involved for the W complex with respect to the Cr and Mo complexes. A similar situation is found in the series of $M(PF_3)_6$ complexes (M = Cr, Mo, W) [24].

In general a small destabilization of the chlorine and bromine lone pairs is measured upon complexation, suggesting that σ-donation is more than compensated by π-interaction.

With increasing electron withdrawing abilities of the ligand L in $M(CO)_5L$, backbonding into the carbonyl 2π-orbital reduces and donation from the 5σ-orbital increases. Because of the antibonding character of both orbitals the C–O bond strengthens, which is nicely demonstrated by the carbonyl stretching frequencies. On the other hand, the 4σ-orbital (approximately lone pair oxygen) turns out to be very sensitive to the mode of bonding. Since the band is quite isolated and very intense in He II, its ionization potential can be determined. So we found a good relation between the equatorial ν(C–O) and the ionization potential of 4σ (see Figure 7). A possible rationalization of this behaviour is that the ionization

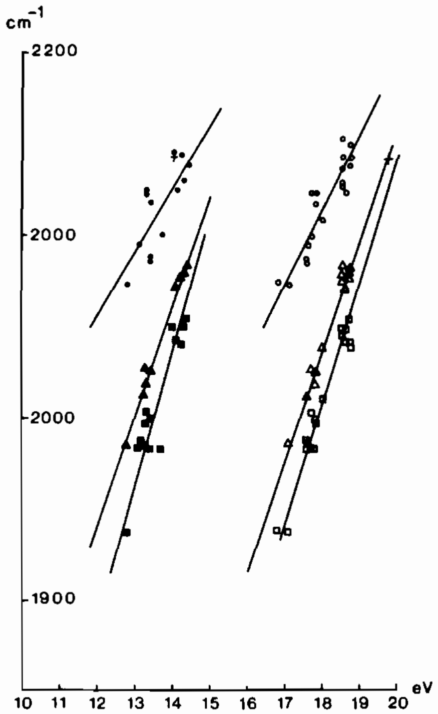

Figure 7. Plot of the equatorial CO stretching vibrations against the energy of the carbonyl 5σ and 4σ-levels in metal pentacarbonyl (○ = A_1, △ = B_1, □ = E, + = free CO). Vibrational data from ref. 20, 21, 26, 27 and ionization potentials from ref. 1, 2, 3, 28, 29.

of 4σ is a measure of the electron density on CO. When the equatorial ν(C–O) are averaged, the free CO molecule fits very well within this series. The ionization potential of 4σ also stresses the similarity in electronic structure between hexacarbonyls and $M(CO)_5PX_3$ (X = F, Cl, Br).

The onset of the carbonyl region from 13–17 eV also shifts to higher ionization potential as the electronegativity of X in $M(CO)_5PX_3$ raises. The onset is tentatively assigned to the 5σ-level. Similar trends have been observed for manganese and rhenium pentacarbonyls. The deviation of the 5σ-level from free CO is attributed to the presence of σ-interaction in the complex.

Intensities

Within the series $M(CO)_5PX_3$ a relative increase in intensity of the bands belonging to the d-orbitals is found in both the He I and He II spectra going from Cr to Mo and W. This so called heavy atom effect has been described for the corresponding hexacarbonyls and for substituted pentacarbonyls of group VII-B metals [28].

Measurements of the photoionization cross section of the 5σ- and 1π-levels in CO show an average decrease of a factor 2.5 going from He I to He II [35]. This explains the results of the hexacarbonyls.

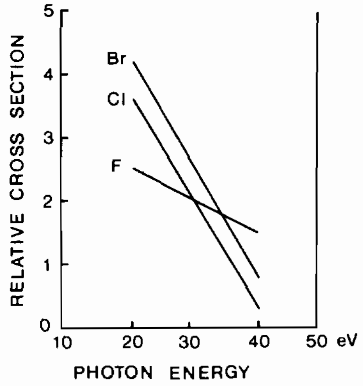

Figure 8. The average cross section of halogen p-orbital relative to the band belonging to the metal d-orbital as a function of the photon energy.

The bands belonging to the d-orbitals will maintain their intensities going from He I to He II in absolute sense.

As is shown in Table III the intensities of the band from the PX_3 moiety will be reduced considerably going from He I to He II.

This reduction of the lone pair phosphorus will be smaller in cases where considerable mixing with the metal d-orbital occurs. The intensity behaviour, however, of this lone pair in the complexes is similar to the intensities in the free ligand (see Table IV and V). The conclusion must be that no important mixing with the metal d-orbitals exists.

Also the relative intensities of the lone pair phosphorus of PF_3 and PCl_3 in the complex can be compared. It turns out that the intensity ratio of σM–PCl_3 to σM–PF_3 is 1.5 in He I and 0.3 in He II. Such different behaviour of the same type of orbital can only be explained by the high influence of the halogen. Indeed the prolonged vibrational progression of this band in the free ligand suggests that the orbital contains a high amount of halogen atomic orbitals.

If it is assumed that the relative intensity of the PF_3 bands in the complex does not significantly deviate from the free ligand, just as has been found for PCl_3 and PBr_3 (see Tables IV and V), one may estimate the intensity of the fluorine lone pairs in the complex from the photoelectron spectrum of free PF_3 and the intensity of the σM–PF_3. The fluorine, chlorine and bromine intensities relative to the intensity of the d-orbital are demonstrated in Figure 8. The strong decrease of chlorine and bromine in going to He II has been reported also for HgX_2 (X = Cl, Br, I) [36]. The different behaviour of fluorine is attributed to its much smaller atomic radius [37].

Conclusions

The low stabilization energy of the phosphorus lone pair upon complexation and the intensity behaviour of the M–P band in going from He I to He II show that σ-donation alone cannot account for the metal–phosphine bond.

The low energy of the metal d-orbitals, the absence of a splitting of the corresponding band in the C_{4v} symmetry of the complex and the reduced spin–orbit coupling constant are consistent with a high amount of π-backbonding.

From the energy of the halogen lone pair it was derived that σ-donation was indeed more than compensated by π-backbonding.

It was deduced:

a) the electron density on the metal increases in the series $PF_3 < CO < PCl_3 \sim PBr_3$.

b) σ-donation increases in the order $PF_3 < PCl_3 \sim PBr_3$

c) the electron density on the metal increases in the order W < Mo < Cr.

The i.p. of the carbonyl 4σ-orbital seems to reflect the charge on CO.

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