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PHOTOELECTRON SPECTROSCOPY IN ORGANOMETALLIC CHEMISTRY *

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Summary

The applications of both UV/PES and X-Ray/PES in the field of organometallics have been reviewed.

UV spectroscopy provides informations on the bonding scheme. Cobalt clusters, alkylgermanium halides, aromatic and alkynyl mercury derivatives, and silacyclanones are used as representative of the potentialities of the method.

X-Ray/PES can be scarcely used for structure determination, but oxidation states, coordination, catalytic effects, and sometimes conformations can be attained that way. Praseodymium complexes of aziridines, organotin complexes of amino acids, aryltricarbonylchromium compounds are used as examples. The chemical nature of vanadium in oil has been recently investigated.

Introduction

Electron spectroscopy became familiar to chemists about 15 years ago. The basic principle is that electrons are emitted by any material which is irradiated by a beam of photons of sufficient energy. Two situations (a) and (b) can occur:

(a) The incident photons have a very large ($>$ 1000 eV) energy and core electrons can be ejected with a kinetic energy so large that interactions between atoms or molecules are negligible. The sample can be an insulating or conducting solid.

The kinetic energy E_k of an emitted photoelectron is given by the well-known photoelectric law, $h\nu = E_k + I + K$, where I is the ionization potential, $h\nu$ the energy of the X-ray photon, and K depends on the spectrometer.

Therefore use is made of a reference line, usually the 1*s* signal of carbon (I 285 eV), so that the binding energy can be obtained from $I - 285 = E_{k(\text{ref})} - E_k$. From tables of I values the identities of the elements present in the sample can be deduced.

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In addition, the value of *I* depends on the chemical environment of the ionized atom, resulting in a chemical shift from which chemical information can be obtained. This technique is known as ESCA spectroscopy or X-PES.

(b) The energy of the incident photon is low, around 20 eV, i.e., in the UV region, and only valence electrons can be reached. The interaction energies are large with respect to the kinetic energy and it is necessary to work with gas samples. The main point is that in this way quantitative data on the orbital diagram are readily accessible. The technique is known as UV-PES.

Both techniques can be applied to organometallic compounds and this will now be discussed.

1. ESCA spectroscopy

The core level binding energies are sensitive to substituent effects, i.e., to the nature of groups directly or indirectly linked to the ionized atom, and this bred great hopes of the technique in the beginning. However, there is an important limitation. The range of chemical shift for a given element is usually very narrow. For example, for tin it is 4.35 eV. The change in binding energy is approximatively proportional to the change in atomic charge, but the proportionality constant is inversely proportional to the atomic radius. This is illustrated in Fig. 1 [1] in which the values of *I* of some typical germanium compounds are placed on the *x*-axis, and the *I* values of the analogous compounds of C, Si, Sn and Pb on the *y*-axis. The slopes of the straight lines obtained give an estimate of the sensitivity of the different atoms, and if the

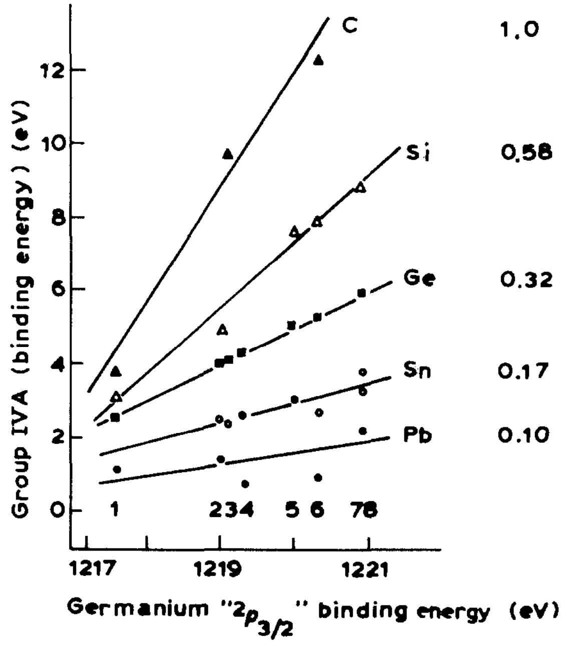


Fig. 1. Relative chemical shift effect in Group IV compounds [4]. Compound types: 1 = M, 2 = $(C_6H_5)_4M$, 3 = Na_2MO_3, 4 = MS, 5 = MS_2, 6 = MO_2, 7 = MF_2, 8 = KMF_6; M = C,Si,Ge,Sn,Pb.

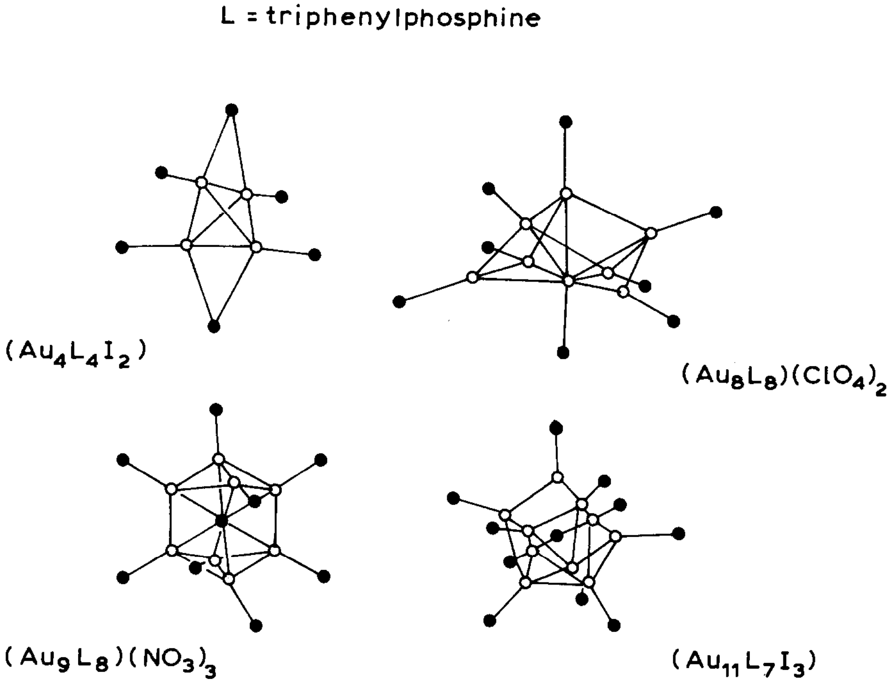


Fig. 2. Typical gold centered and non-gold centered gold complexes.

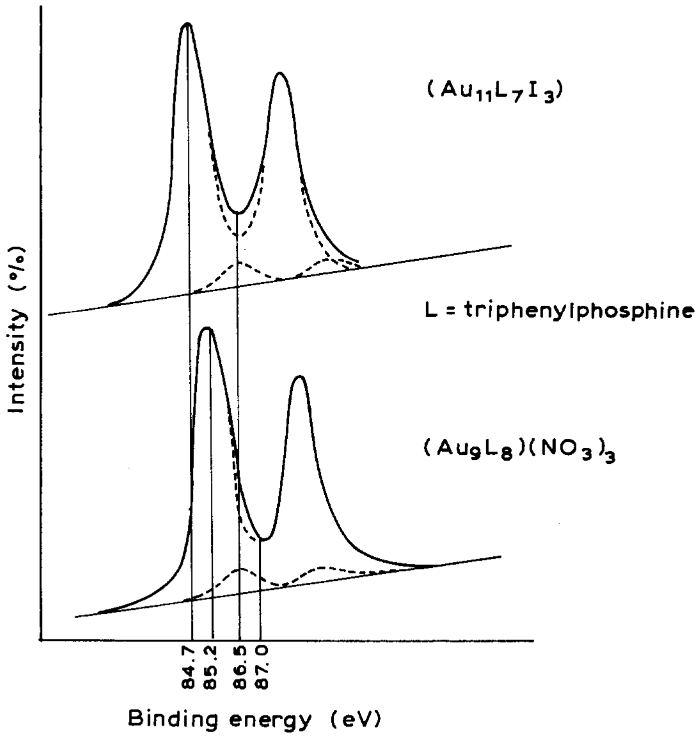


Fig. 3. X-ray-PES spectra of gold triphenylphosphine complexes.

sensitivity of carbon is taken as unity, that of tin is only 0.17. This result has to be kept in mind.

Structure assignment

It is only in favourable cases that X-PES can provide information about the chemical structure, for example, in the case of gold complexes. In Fig. 2 are shown the molecular structures of some gold triphenylphosphine complexes. Some are gold-centered (Au_9L_8 and $Au_{11}L_7I_3$) and some are not. In Fig. 3 are shown [2] the X-PES spectra ($Au_{4f_{7/2}}$) of the two gold-centered complexes. From the experimental band contour it is possible to extract the gaussian components and to reveal a doublet due to the central gold atom. It is noteworthy that the corresponding ionization potential is almost the same for both compounds.

The next example is taken from the chemistry of carbonyl compounds. The problem was to assign a correct formula to a complex containing the three metal atoms Fe, Ge, Ni, and a number of CO and C_5H_5 ligands. The oxygen 1*s* signal from the CO ligands is shown in Fig. 4. By measuring the relative intensities of the observed peaks it is easy to show that there are two CO groups on one metal atom and one on another atom. Comparison of the observed shifts with those of $Ni(CO)_4$ and $Fe(CO)_5$, show that the partial structures $Fe(CO)_2$ and Ni(CO) are present. This result illustrates the optimistic hope chemists had of using ESCA as a super NMR, working with any element and without complicating couplings.

Determination of complexation sites

This is a more commonly encountered application, and it is typified by the example illustrated in Fig. 5.

The problem was raised by organic NMR spectroscopists who used shift reagents

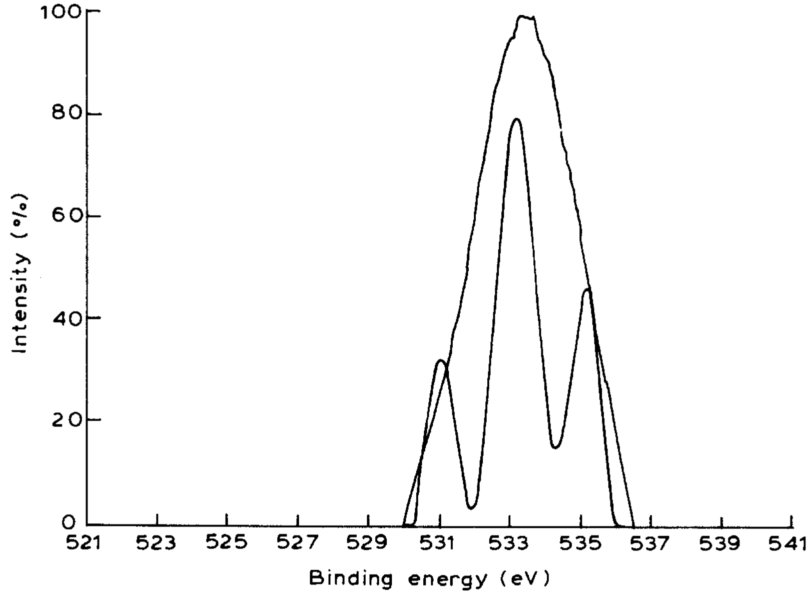


Fig. 4. X-ray-PES spectrum of $(C_5H_5)(CO)_2Fe{-}GeBr_2{-}Ni(CO)(C_5H_5)$.

to study oxiranes and oximes in the cyclohexane series. To assign a stereochemical structure to the compounds it was necessary to know if the metal was bound to oxygen or to nitrogen. We proved that with oxime ligands the site of complexation was mainly oxygen, the resulting ESCA shift of the oxygen 1*s* peak being 1 eV to lower energy. In the oxiridine series the situation is clearly different. When the α-positions bear methyl groups, the complexation site is exclusively nitrogen, resulting in a shift to lower energy of 1.1 to 2.4 eV; when there is a CH_3 group next to the oxaziridine function, there is some complexation on oxygen in addition to that at nitrogen.

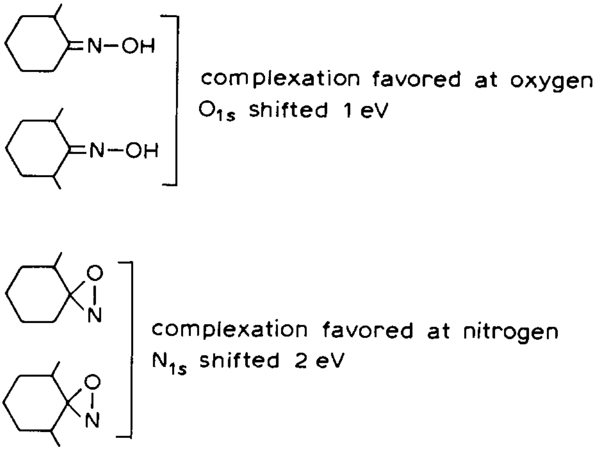


Fig. 5. Complexation of oximes and oxiridines by NMR shift reagents.

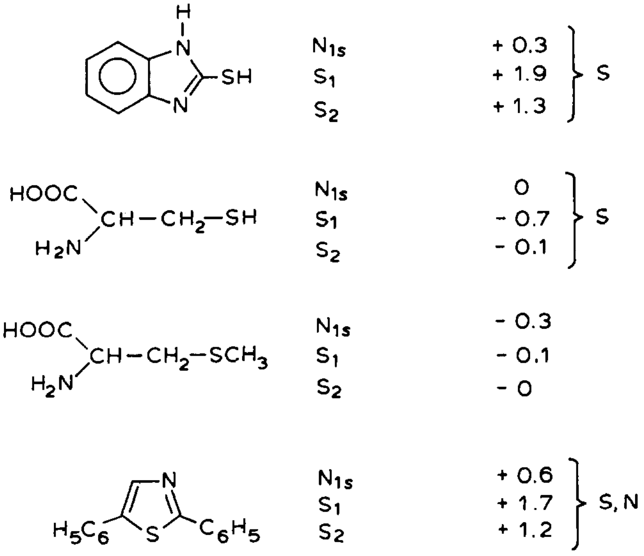


Fig. 6. Site of complexation (S or N) of Bu_3SnCl with sulfur and nitrogen ligands, showing shifts (in eV) in the values of *I*.

Another example is a study of formation of complexes between $Sn(C_4H_9)_3Cl$ and amino acids. The interest in this study was the fact that tin compounds are usually toxic. We thought that a pentacoordinated complex between tin and a suitable group in a protein chain might give rise to the observed toxicity [3]. Two questions were involved: the existence of such complexes, and the site of complexation. The results are summarized in Fig. 6 and reveal the following points.

Two sets of compounds have to be considered, exemplified by 2-mercaptobenzimidazole (**1**) and cysteine (**2**); both contain a free SH group, but they behave differently. For **1** all the ionisation potentials are shifted to higher energy, while for **2** only the S signals are shifted, and to lower energy. Complexation through either nitrogen or sulfur is expected to cause a shift towards higher values of the ionisation potential of the element acting as donor, but in fact a low energy shift is often observed. The conclusion is that complexation occurs at the SH group when it is present. We compared compound **1** with another sulfur-nitrogen aromatic molecule, diphenylthiazole, and the results were very similar: S_{2p} -1.7, N_{1s} $+0.6$, Sn_{3d} $+0.3$. We believe that the aromatic compound acts as a bidentate ligand and that a hexacoordinated tin complex is formed.

When the compound does not contain an SH group but sulfur atoms are still present, in the form of $S{-}CH_3$ or S–S groups, definite evidence is lacking of the formation of a complex, either at nitrogen or sulfur. We conclude that formation of complexes with amino-acids requires the presence of free SH groups. In no case were NH_2 groups basic enough to coordinate to tin.

Examination of conformation equilibria

Very fine details can be sometimes obtained from ESCA and the next example concerns a conformation equilibrium. Arenechromium carbonyl compounds of the type $ArCr(CO)_3$ raise two questions: (i) the real nature of the benzene–Cr and

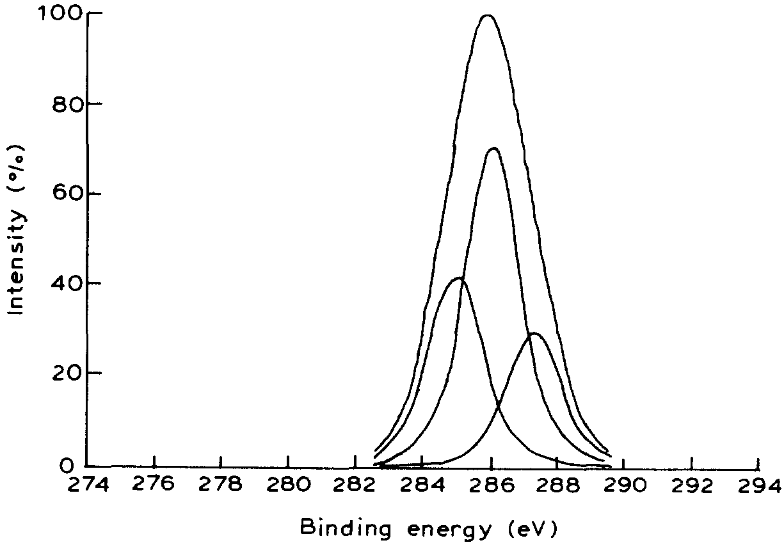


Fig. 7. X-ray-PES C_{1s} signal of $C_2H_5C_6H_5Cr(CO)_3$.

CO–Cr bonds, and (ii) the conformation of the benzene ring with respect to the Cr–CO bonds. These two questions can be answered by ESCA.

The C_{1s}, O_{1s} and Cr_{3d} ionization potentials were measured for the series X-$C_6H_5Cr(CO)_3$. In Fig. 7 are shown the C_{1s} signals of $EtC_6H_5Cr(CO)_3$ and the resolved signals of the residual atmosphere, the benzene ring ethyl group, and the carbonyl carbon atoms. The intensities of the last two are in the required 8/3 ratio.

Figure 8 shows the I vs. σ_p^+ correlation. As the electron density increases around a given atom, the ionization potential of an electron in a given level of this atom, decreases [4] and so the following conclusions can be drawn. When the electron-releasing effect increases (σ_p^+ decreases) the ionization potential of Cr_{3s} decreases, i.e., the chromium atom becomes more negative (less positive). This can be accounted for in two different ways: (i) an increase in electron density at the chromium atom due to a larger transfer of electrons from the ring to the empty chromium orbitals; and (ii) a strengthening of the CO–metal bond, and a shift of the electrons of the bond towards the metal.

If the first hypothesis is correct, the aromatic carbon C_{1s} ionization potentials should vary in the opposite way to those of Cr_{3s}, as is the case, and this means that there is more electron density transferred from the ring to the chromium atom than

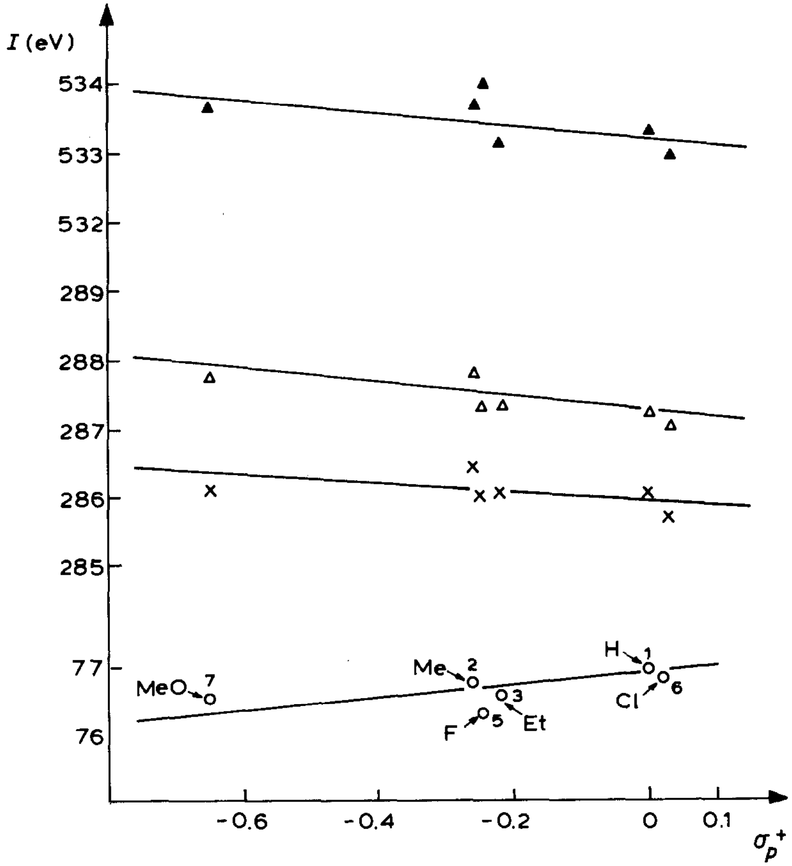


Fig. 8. Variation of the O_{1s}, C_{1s}, Cr_{3d} ionization potentials with σ_p^+ of X in the series X-$C_6H_5Cr(CO)_3$.

from X to the ring. Therefore the ionization potential of the oxygen or carbon of the carbonyl groups is expected to vary in the same way as Cr_{3d}, which is not the case. According to Fig. 8, when the electron density on the chromium atom increases the electron density on C and O decreases. This means that when some electron density is induced in the chromium atom orbitals by the electron releasing effect of X, it is transmitted to the carbonyl ligand through the *d* orbitals of chromium, but in return the carbonyl–metal bond is strengthened, increasing the partial negative charge on the chromium atom and decreasing the partial charge on both C and O.

We now turn to polysubstituted compounds. This means that we have to cope with problems of conformation. This issue has already been investigated by variable temperature proton magnetic resonance and the results are shown in Fig. 9. When only one substituent is present its electronic effect determines the preferred conformation, i.e. the *d* orbitals are eclipsed by the position of higher electron density on the ring, as shown in **a**; this conformation will be referred to as eclipsed. When there are many substituents there is a competition between steric and electronic effects, as shown in **b**. When the substituents are arranged in a fully symmetrical way the preferred configuration is the staggered one, **c**, as in benzenetricarbonylchromium itself.

All the structures which allow overlap of *d* orbitals with the benzene positions of higher electron density involve steric interaction between CO and CH_3.

In cases **2** and **11** (Fig. 10), the non-methylated positions *ortho* or *para* to the methyl groups are very efficient in forming bonds using chromium *d* orbitals. Therefore the steric effect arising from eclipsed CO and methyl groups is more than cancelled by electronic effects. In **9** the electronic effects are less significant, and steric interactions can be reduced by assuming the staggered conformation **B**. Let us suppose that **9** has the conformation **B**. The experimental ESCA shifts for **9** should be similar to these of **1**, and **2**, **10** and **11** should form a continous series. If the real conformation is **A**, the values of *I* observed for **9** should be close to those measured for **10** and the same as for **2** and **11**.

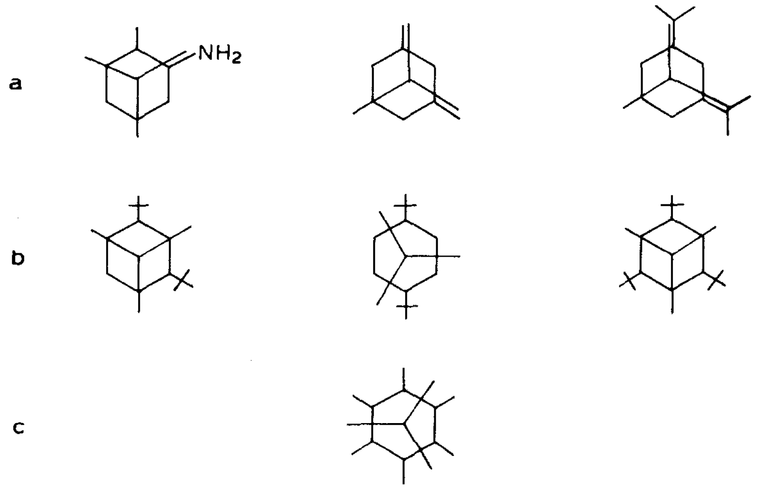


Fig. 9. Conformation of some arenechromium tricarbonyls as determined by ^1H NMR.

In Fig. 10 are shown the values obtained for compounds **1**, **2**, **9**, **10** and **11**, and it is clear that hypothesis **A** is the better.

2. UV Photoelectron spectroscopy

Electron interactions and bonding

The question of *d* orbital participation has been a matter of discussion for many years. We now consider how UV-PES can help to clarify the matter.

Let us take as the first example $CH_3OSi(CH_3)_3$ (1) and $(CH_3)_3SiOSi(CH_3)_3$ (2). The useful part of each spectrum is shown in Fig. 11. A doublet appears where the signal of the oxygen lone pair is expected, revealing that there is conjugation with the available Si *d* orbitals. Moreover when two $OSi(CH_3)_3$ groups are present the splitting is doubled, which means that the two $Si(CH_3)_3$ group can both meet the orientation conditions required for conjugation and therefore assume a staggered conformation with respect to one another.

	CO	O	Cr
1	287.2	533.3	76.7
9	287.2	532.9	75.8
2	287.8	533.7	75.7
10	287.3	533.3	76.1
11	287.9	533.8	76.1
2	287.8	533.7	75.7
11	287.9	533.8	76.1
9	287.2	532.9	75.8
10	287.3	533.3	76.1

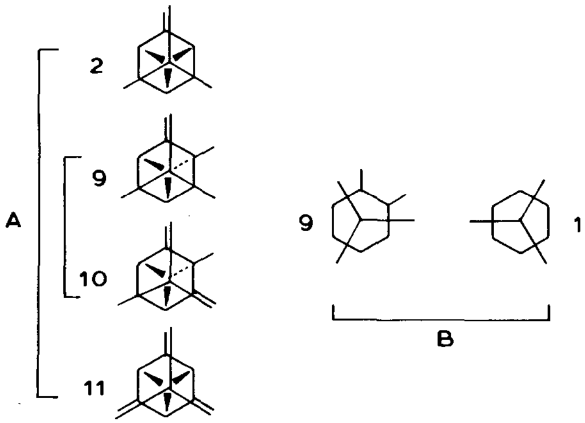


Fig. 10. Ionization potentials and conformations of some arenechromium tricarbonyls.

As another example we take $Hg(C_6H_5)_2$. The possible interaction is between the Hg $5d$ and sp^2-ring orbitals. Figure 12 shows the He(I) and He(II) spectra [5]. The 9 eV band corresponds to the 9.3 band of benzene (assigned to e_{1g} orbitals) and is assigned to the HOMO of the two phenyl rings, the quasi degeneracy of these levels indicates almost no through-metal interactions.

Comparison of the He(I) and He(II) spectra reveals the π character of peaks 1, 3 and 5, and even more clearly the Hg character of peaks 6 and 8. The closeness of the bands observed in $Hg(CH_3)_2$ and $Hg(C_6H_5)_2$ suggests a similar $5d$ electron distribution and argues against any interaction between the C_6H_5 and Hg $5d$ orbitals.

Comparison of He(I) 21.21 eV and He(II) 42.42 eV spectra provides some easily interpreted information. Going from He(I) to He(II) decreases the intensity of mainly π bonds. Let us consider [6] $Co(CO)_6HC{\equiv}CH$, for which Fig. 13 shows both the He(I) and He(II) spectra. It is clear that band **B** is a ligand band and **A** mainly a metal band. **C** is assigned to CO ligands by comparison with the unsubstituted cobalt carbonyl $Co_2(CO)_8$. The value of I for the C_2H_2 band is about the same as for C_2H_2, which means that bond formation is compensated by back-donation.

Intramolecular interactions

Some problems of intramolecular interactions in relation to conformation equilibria can also be investigated by UV-PES spectroscopy. We have examined some silacycloalkanones.

Figure 14 shows the spectra of dimethylsilacyclohexanone and cyclohexanone [7]. In any ketone the first band (low values of I) results from the ionization of an electron of the free pair of the oxygen, as indicated by the fine structure due to the C=O vibration. The corresponding ionization potential, 9.19 for cyclohexanone, decreases as the ring-size increases, to reach 8.96 for an eleven-membered ring (see Fig. 15).

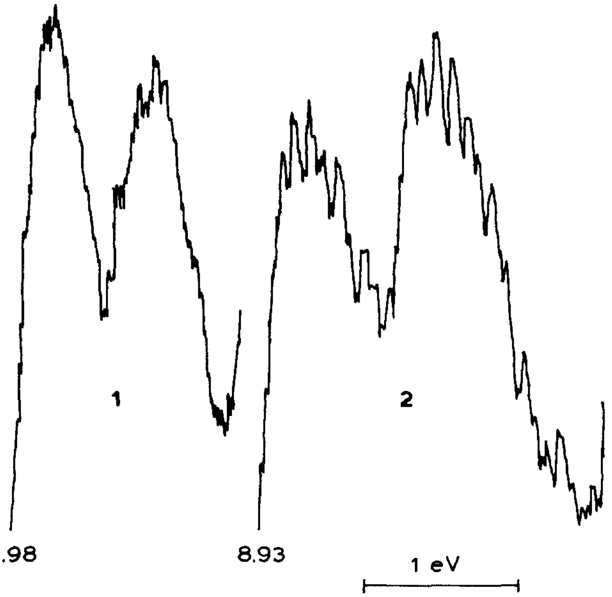


Fig. 11. UV-photoelectron spectra of $CH_3OSi(CH_3)_3$ (**1**) and $(CH_3)_3SiOSi(CH_3)_3$ (**2**).

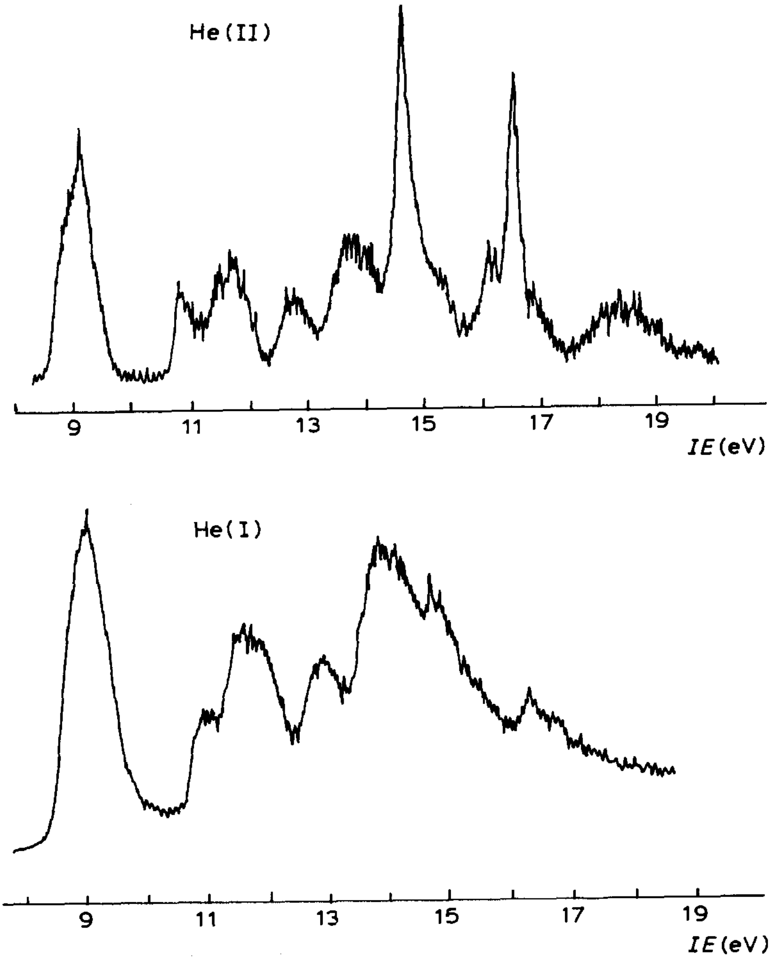


Fig. 12. He(I) and He(II) UV-photoelectron spectra of $Hg(C_6H_5)_2$.

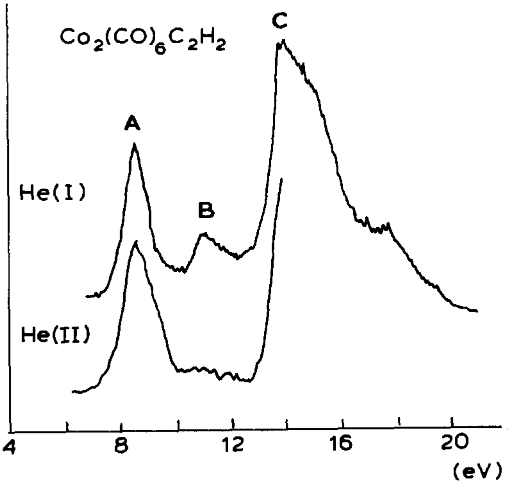


Fig. 13. He(I) and He(II) UV-photoelectron spectra of $Co_2(CO)_6C_2H_2$.

In the silicon series, the Si–C bands, which are between 10 and 11.5 eV, do not obscure the C=O region, and the first band is again readily assigned to the free pair of the oxygen. The next three bands are assigned to the ionization of electrons located on C–Si bonds by analogy with the spectra of tetramethylsilane.

Ring enlargement should destabilize any of the highest occupied orbitals, *n*(O), (C–C) and (C–Si), and the results for cycloalkanones are in agreement with this idea. On going to silacycloalkanones a particular feature is observed, namely that the first ionisation potential is lowered by ring expansion much less than in the cycloalkanone series. As the hyperconjugative effect of the alkyl part of the ring is the same, this effect can only be assigned to a *n*(O)–3*d* interaction, which is effective in the medium-size rings in which the flexibility allows a folded conformation in which O and Si are sufficiently close to each other. This interaction allows a small charge transfer from the oxygen orbital to the empty 3*d* orbitals, with the consequence of increasing the first ionization potential, assigned to *n*(O) electron pairs, compared to the corresponding value in the carbon series. The ionization potential of the σ(C–Si) electrons should decrease correspondingly, as is observed.

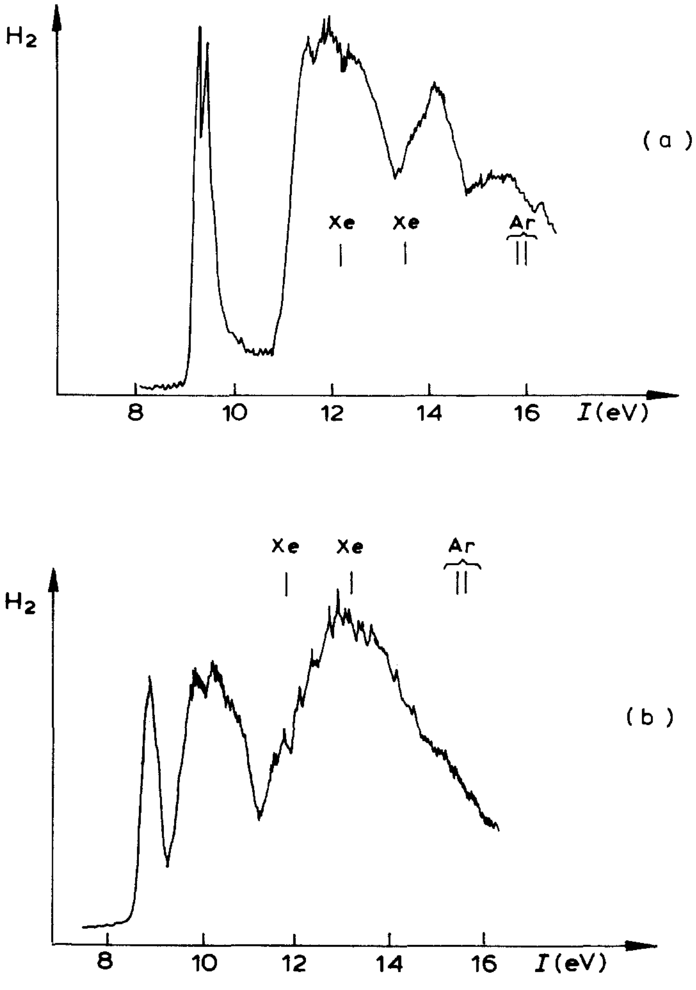


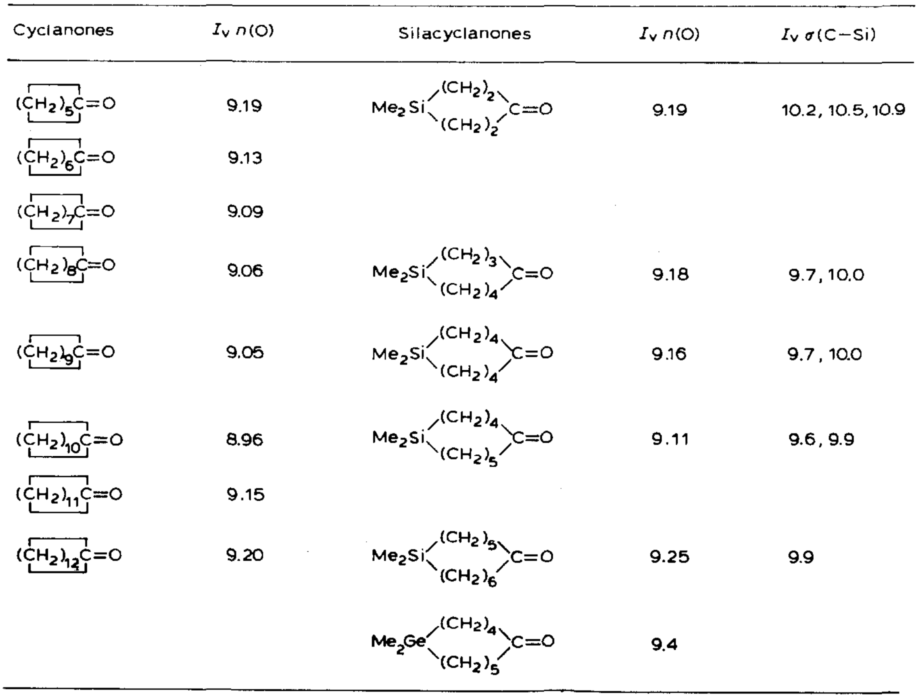
Fig. 14. UV-photoelectron spectra of cyclohexanone (a) and dimethylsilacyclohexanone (b).

Ring strain effects

For the cyclostannane series we do not tackle the problem of *d* orbital participation but instead try to account for the observation that under attack by nucleophilic reagents, such as bromine, the rings open; for example, dimethyl(5-bromopentyl)tin bromide is obtained from dimethylstannacyclohexane. We had prepared a series of stannacycloalkanes, and we wondered whether it would be possible to observe any ring strain effect by PES by measuring the ionisation potentials of exo and intracyclic tin–carbon bonds.

The PE spectra of some dimethylstannacycloalkanes [8] are shown in Fig. 16, and they are all remarkably similar. In all cases the photoelectron transitions appear in two groups: a single, well-defined low ionization energy band with a fine structure, and a broad ionization region at higher energy. The low energy band can be assigned to the ionization of the exocyclic Sn–C bond comparison with $Sn(CH_3)_4$. The value observed for the first ionization potential must be discussed, as well as the multiplicity. The fact that a single peak is observed with ethyltin compounds shows that the appearance of three peaks is associated with the methyl groups. This is clearly a Jahn-Teller effect. The distorting effect and therefore the splitting of the first band are expected to vary inversely with the distance between interacting groups, i.e., the methyl groups.

The value of the first ionization bands are listed in Fig. 17, from which the following conclusions can be drawn: (a) the tin–methyl bond is the most easily ionized in the stannacyclohexane (whatever component of the band is chosen for comparison); (b) the methyl groups, on the basis of Jahn-Teller effect, are closer in



Cyclanones	I_v n(O)	Silacyclanones	I_v n(O)	I_v σ(C–Si)
$(CH_2)_5C{=}O$	9.19	$Me_2Si\genfrac{<}{>}{0pt}{}{(CH_2)_2}{(CH_2)_2}C{=}O$	9.19	10.2, 10.5, 10.9
$(CH_2)_6C{=}O$	9.13			
$(CH_2)_7C{=}O$	9.09			
$(CH_2)_8C{=}O$	9.06	$Me_2Si\genfrac{<}{>}{0pt}{}{(CH_2)_3}{(CH_2)_4}C{=}O$	9.18	9.7, 10.0
$(CH_2)_9C{=}O$	9.05	$Me_2Si\genfrac{<}{>}{0pt}{}{(CH_2)_4}{(CH_2)_4}C{=}O$	9.16	9.7, 10.0
$(CH_2)_{10}C{=}O$	8.96	$Me_2Si\genfrac{<}{>}{0pt}{}{(CH_2)_4}{(CH_2)_5}C{=}O$	9.11	9.6, 9.9
$(CH_2)_{11}C{=}O$	9.15			
$(CH_2)_{12}C{=}O$	9.20	$Me_2Si\genfrac{<}{>}{0pt}{}{(CH_2)_5}{(CH_2)_6}C{=}O$	9.25	9.9
		$Me_2Ge\genfrac{<}{>}{0pt}{}{(CH_2)_4}{(CH_2)_5}C{=}O$	9.4	

Fig. 15. Vertical ionization potentials of cycloalkanones and silacycloalkanones.

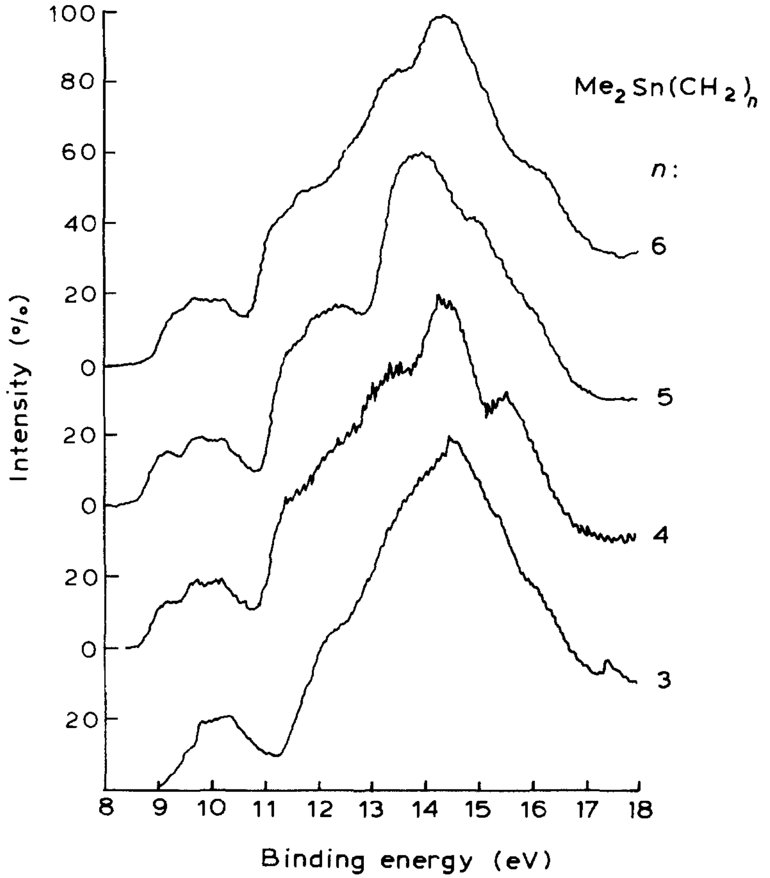


Fig. 16. UV-photoelectron spectra of some dimethylstannacycloalkanes.

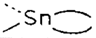
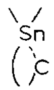
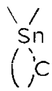
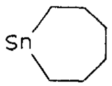
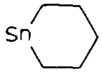
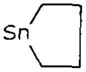
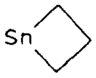
		R = Me 						R = Et		
	n	1	2-1	2	3-2	3	3-1			
	6	9.40	0.40	9.80	0.50	10.30	0.9	14.6	9.50	14.6
	5	9.15	0.45	9.60	0.65	10.25	1.10	13.8	9.46	13.6
	4	9.20	0.52	9.72	0.48	10.25	1.05	13.4	9.58	13.4
	3	9.65	0.25	9.90	0.45	10.25	0.7	13.8	—	—

Fig. 17. Ionization potentials of dimethyl- and diethyl-stannacycloalkanes.

stannacyclohexane than in any other compound, which means that the C–Sn–C angle is the largest in the series.

A change in ring size is probably accompanied by a change in hybridization of the tin atom. An increase in the value of *I* means an increase in *s* character. If the *s* character of the exocyclic Sn–C bond increases the C–Sn–C angle in the ring will decrease, so opening the C–Sn–C exocyclic angle and increasing the distance between the two methyl groups and, therefore, decreasing the interaction. The largest value of *I* then corresponds to the smallest Jahn-Teller effect. The Jahn-Teller effect is largest and the value of *I* smallest for the stannacyclohexane. Thus, the ring strain affecting the tin–carbon bonds is smallest in the stannacyclohexane. Consistently the (Sn–C) ionisation potential is close to that of $SnMe_4$: 9.60 vs. 9.62.

We have also investigated by UV-PES the conformation of stanna-1,3-dithiolanes, whose main structural element is a five-membered ring containing the S–Sn–S moiety [9]. Our aim was to elucidate the preferred conformation of this ring.

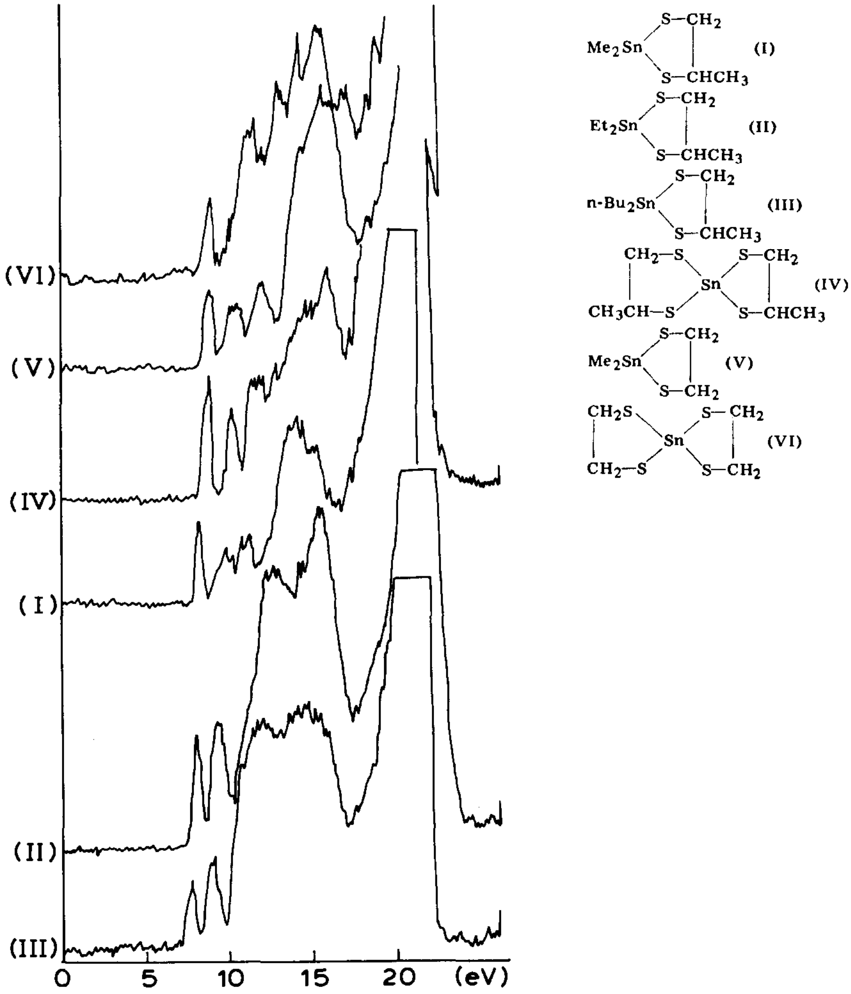


Fig. 18. UV-photoelectron spectra of dialkylstanna-1,3-thiolanes.

Preliminary proton NMR results did not allow a clear decision between a rigidly planar and a highly flexible ring. Previous investigations on dimethylthiolanes led to the conclusion that in open-chain compounds the most stable conformation is a planar S–M–S arrangement. Assignments of signals were based on CNDO calculations on carbon and silicon compounds. The main feature was that the first two signals were combinations of sulfur lone pairs (bonding n^+ and antibonding n^-), the splitting of which decrease, and eventually vanish when the ring is planar. The spectra shown in Fig. 18 are the UV-PES spectra of dialkylstanna-1,3-thiolanes and

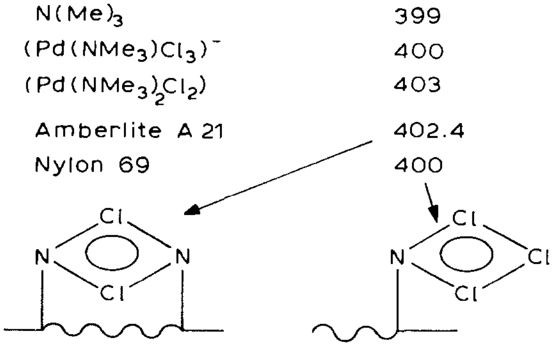


Fig. 19. N_{1s} ionization potentials in supported palladium based catalysts.

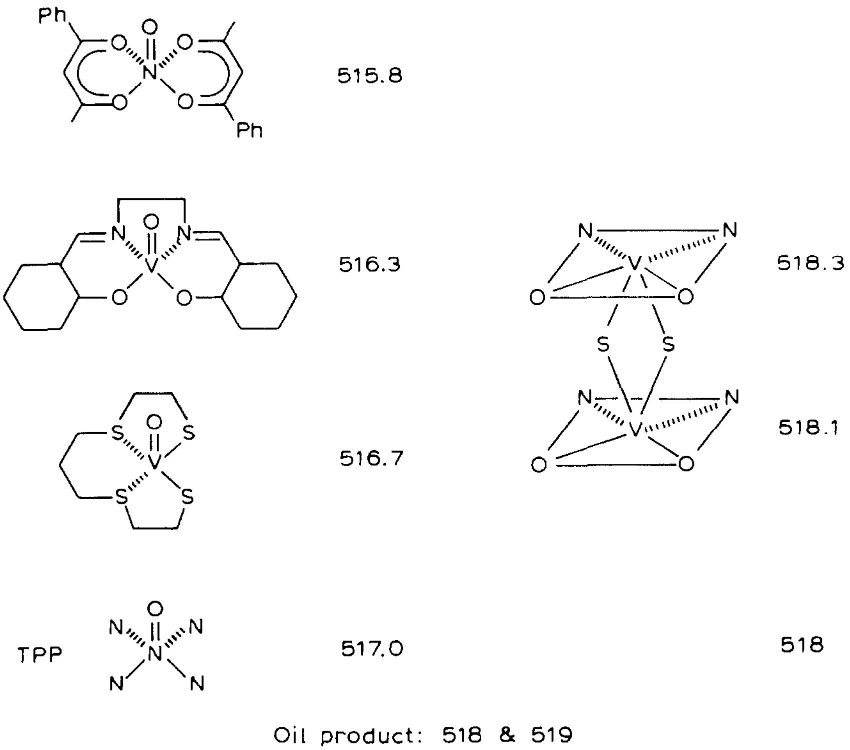


Fig. 20. X-ray ionization potentials for some vanadylporphyrins.

the corresponding spiranes. In all cases the first band is a broad signal assigned to sulfur lone pairs, and so the stannathiolane ring is not planar. It is in the spirane, with two five-membered rings, that the ring is the closest to planarity.

I will end with two applied examples. The first concerns catalysis by palladium complex salts on polymeric supports containing amino groups. As shown in Fig. 19, palladium can be attached to the resin by one or two nitrogen atoms. On treating K_2PdCl_4 with $N(CH_3)_3$ a mixture of $[PdCl_3N(CH_3)]^-$ and $[PdCl_2(N(CH_3)_3)_2]$ was prepared. The X-PES spectrum shows N_{1s} bands at 400 and 403 eV (also at 399 eV due to excess free amine). Two catalysts were then examined, one on Amberlite A-21 and the other on nylon 69. The observed N_{1s} ionization potentials are 402.4 and 400.8, respectively, thus establishing the structure of the supported Pd catalyst.

The second example concerns the correlation between the sulfur, vanadium, and porphyrin content of crude oil. Some hypotheses have been put forward suggesting that sulfur combines with vanadylporphyrins, and that in addition the vanadylporphyrins are complexed by condensed polyaromatic products. We have tried to contribute to the solution of the problem by an ESCA study based on the $V_{2p3/2}$ peak. We started by examining some model compounds similar to porphyrins and their sulfur-bridged dimers. For the vanadyl models, I for $V_{2p3/2}$ is ca. 516–517 eV. For the two dimers investigated it goes up to 518 eV, while for crude Venezuelian oil two peaks are observed at 518 and 519, which we assign to free and complexed thio-dimers (see Fig. 20).

Conclusion

Bot ESCA and UV photoelectron spectroscopy can provide insight into some problems of structure and bonding, but full assignments of the ionization potentials usually require theoretical treatments which are not available for heavy metals. In such cases it is necessary to rely on correlations with similar structures involving smaller numbers of electrons.

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