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He(I) and He(II) Photoelectron Spectra of *trans*-[Pd(PEt$_3$)$_2$X$_2$] Complexes

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Pd(I) and Pt(II) square planar complexes of the type [M(PR$_3$)$_2$(X)(Y)] have been the object of several investigations concerning their reactivity [1, 2]. Qualitative electronic structure considerations have often been invoked to discuss their reaction mechanisms, but no experimental evidence of their valence electronic levels has yet been reported. The gas-phase Ultraviolet Photoelectron Spectroscopy (UV–PES) furnishes a straightforward way to measure the electronic energy levels, but, until now, only preliminary PE data on some Pt(II) complexes have been reported [3]. For this reason we have undertaken a comprehensive PE and theoretical study on the series *trans*-[M(PEt$_3$)$_2$(X)(Y)] where M = Pd, Pt and X, Y = halogen, alkyl, hydrogen. We report here the He(I) (21, 21 eV) and He(II) (40.81 eV) excited PE spectra of *trans*-[Pd(PEt$_3$)$_2$Cl$_2$] and *trans*-[Pd(PEt$_3$)$_2$Br$_2$].

Figures 1 and 2 show the PE spectra, and the pertinent Ionization Energies (IEs) are reported in Table I. Spectra were measured on a Perkin-Elmer PS18 spectrometer using a heated inlet probe system in the 80–90 °C temperature range. The spectrometer was connected on-line with a Minc-23 (Digital Equ.) computer. The IE scale was calibrated by reference to peaks due to mixed inert gases (Xe, Ar) and to 1 s^{-1} He ionization.

The bands we discuss in the present paper are those labelled alphabetically in the Figures (up to 11 eV); the higher IE region shows a broad envelope whose ionizations are poorly resolved. On the other hand they are not relevant for the discussion of the bonding of the complexes, since they mainly originate from PEt$_3$ localized σ MOs. The ionizations from the inner Pd–P and Pd–Cl bonding MOs could however be hidden under this broad band.

TABLE I. Ionization Energies (eV) of *trans*-[Pd(PEt$_3$)$_2$X$_2$] Complexes.

label	X = Cl	X = Br
A	8.08	7.89
B	8.52	8.13
C	9.81	9.02
C′	–	9.40
D	10.54	10.8

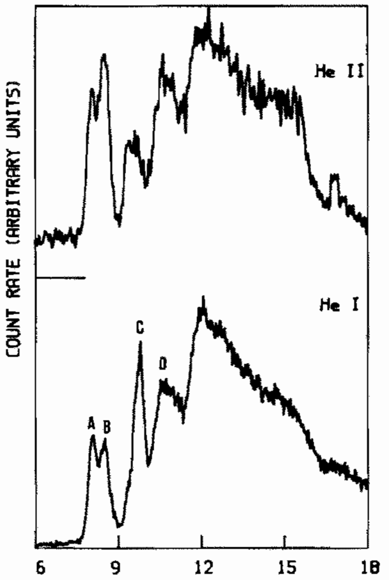

Fig. 1. He(I) (bottom) and He(II) (top) PE spectra of *trans*-[Pd(PEt$_3$)$_2$Cl$_2$].

The following experimental criteria can be used to assign the lower IE region:

(i) The comparison between the He(I) and He(II) intensities. In fact the well-known behavior of the photoionization cross-sections [4] on switching from the He(I) to the He(II) source allows us to identify the bands having high 'd' metallic character as those increasing in intensity in the He(II) spectrum. On the other hand, the 3p chlorine based MOs suffer a marked intensity decrease.

(ii) The comparison with the PE spectra of the whole series of complexes containing the *trans*-M(PEt$_3$)$_2$ subunit [5].

(iii) The well-known IE shift of the halogen based MOs on going from chlorine to bromine [4].

On this basis we propose to assign bands A and B in both complexes to ionizations from 4d metal based MOs; the decrease of band A with respect to B in

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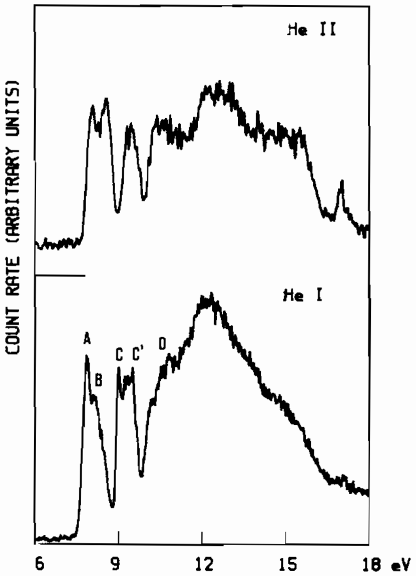

Fig. 2. He(I) (bottom) and He(II) (top) PE spectra of *trans*-$[Pd(PEt_3)_2Br_2]$.

their He(II) spectra indicates a higher 'd' character for the latter. Bands C and C′ are associated with MOs having high np halogen character whereas band D, almost unshifted in the whole series of *trans*-$[M(PEt_3)_2(X)(Y)]$ complexes [5], is associated to phosphorus lone-pairs. *Ab initio* pseudo-potential calculations are in progress and their results, together with more detailed assignments, will be reported in a forthcoming full paper. The most important result we anticipate here concerns the nature of the upmost occupied MOs for the neutral complexes: in contrast with the PE evidence, they are not localized on the central metal atom but are delocalized over the ligand. This means that large relaxation energies are associated with the 'd' ionizations (breakdown of Koopmans' theorem [6]). Consequently, the conclusions concerning the chemical reactivity derived by Behan *et al.* [3] on the basis of PE data of similar complexes seem to be at least questionable.

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