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ESCA and X-Ray Spectral Study of Pd(0), Pd(I) and Pd(II) Compounds with Triphenylphosphine Ligands

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So far a number of papers concerning the X-ray photoelectron study of Pd(II) and Pd(I) compounds have been published (*e.g.* [1,2]). Hitherto Pd(0) and in particular Pd(I) compounds virtually have not been extensively studied by ESCA methods. This paper presents results of the ESCA and X-ray spectral investigations of Pd(0), Pd(I) and Pd(II) compounds. The technique of measurements was similar to the previously used one [3, 4].

L_2Pd_2 was synthesized [5] by the reduction of complex #9 (see Table I) with molecular hydrogen in CH_2Cl_2 (obtained values: Pd 28.0, P 8.2, C 58.0, H 4.7%; molecular weight 690, $C_{36}H_{30}P_2Pd_2$. Calculated: Pd 28.7, P 8.4, C 58.5, H 4.1%, molecular weight 737). $L_2Pd_2(OAc)_2$ was obtained [5] by the interaction of L_2Pd_2 with compound #9 in CH_2Cl_2 (obtained values: C 56.2, H 4.6%, molecular weight 800, $C_{40}H_{36}O_4P_2Pd_2$. Calculated: C 56.1, H 4.2%, molecular weight 855). Complexes ##2,6,8,9 were synthesized by techniques published elsewhere [6–8].

TABLE I. Binding Energy Values, eV, and Oxidation Numbers, N.

#	Compound	$Pd3d_{5/2}$	P2p	N
1	Pd	335.8		0
2	L_4Pd	336.2	131.3	0
3	L_2Pd_2	336.8	131.2	0
4	$L_2Pd_2(OAc)_2$	337.1	131.2	1
5	$[LPd(PPh_2S)]_2$ [a]	337.0		1
6	L_2PdCl_2	338.2	131.4	2
7	$[Pd(OAc)_2]_n$	338.8		2
8	$L_2Pd(OAc)_2$	338.1	131.4	2
9	$[LPd(OAc)_2]_2$	338.5	131.7	2

[a] Ref. 2.

Table I shows data on the energy levels of inner electrons. Similar to the case of Pt compounds [3] the increase of $Pd3d_{5/2}$ binding energy with oxidation number was observed although there are no well defined boundaries between the regions of $Pd3d_{5/2}$ energy values for different oxidation numbers N (see data on Pd(0) and Pd(I)). The high conformity of the shifts of Pd3d and Pt4f lines (which have been obtained earlier for similar compounds of Pd(II) and Pt(II) [1, 2]) was observed also for Pd and Pt compounds with oxidation numbers of 0, I and IV (see Table II compiled from present data and from [1, 3] and references therein). In cases where different data exist they were averaged. The shift of $Pd3d_{5/2}$ line in the compound as compared with its position in a metal is about 10 per cent more than for the $Pt4f_{7/2}$ line in a similar compound.

TABLE II. Shift values for Pd and Pt Lines, eV.

Compound	ΔPd3d	ΔPt4f	N
M [a]	0	0	0
ML_4	0.4	0.4	0
$[LM(PPh_2S)]_2$	1.2	0.7	1
L_2MCl_2	2.4	2.1	2
$K_2M(NO_2)_4$	3.2	3.0	2
K_2MCl_6	4.7	4.4	4
K_2MF_6	7.3	6.5	4

[a] M = Pd, Pt.

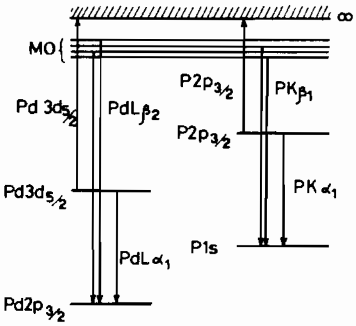

Fig. 1. The diagram of transitions.

Most investigated compounds include L = PPh_3 ligands. The P2p value for a free L is 130.9 eV. The rise of P2p due to coordination suggests a certain decrease of electron density on the P atom *i.e.*, the σ-donor properties of L are somewhat more pronounced than the π- acceptor ones.

The σ-donor properties of L may be demonstrated clearly using X-ray spectroscopy data. The $PK\beta_1$ lines (transition from molecular orbitals to P1s level) and $PdL\beta_2$ lines (transition from molecular orbitals to

TABLE III. Composition of Molecular Orbital Levels, %.

Levels of		Maximum in PKβ_1	OPH$_3$/PH$_3$						OPH$_3$	
OPH$_3$	PH$_3$		P3s		P3p		P3d		O2s	O2p
7a$_1$	5a$_1$	A	1	17	20	71	2	–	12	58
2e	2e	B	–	–	50	47	1	6	–	18
6a$_1$	4a$_1$	C	50	66	10	3	1	–	6	3

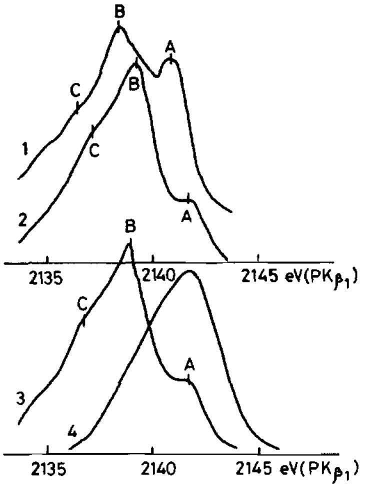

Fig. 2. X-ray spectra: 1,2,3 are PKβ_1 spectra of L, L$_2$Pd(OAc)$_2$, L$_2$PdCl$_2$; 4 is the PdLβ_2 spectrum of L$_2$PdCl$_2$.

Pd2p$_{3/2}$ level) were studied in the compounds ##2–4, 6, 7. Some of obtained data are presented in Fig. 2.

According to selection rules the PKβ_1 line intensity reflects the contribution of P3p orbitals to the wave function of the molecular orbitals [9]. In particular A, B and C maxima in a free L (Fig. 2) are proportional to the contribution of P3p orbitals to different levels, *viz.* A: to a$_1$ level (the lone electron pair of P atom); B: to e-level (P–C σ-bond); and C: to deeper levels of a$_1$ and e types (see *e.g.* the interpretation of PKβ_1 spectrum of R$_3$P in [10]). Upon coordination the relative intensity of A maximum drops drastically thus manifesting the transfer of lone electron pair density from P atom to the 4d level of Pd atom. Indeed the calibration of PKβ_1 and PLβ_2 spectra to a common energy scale on the basis of experimental values of X-ray transition energy (PdLα_1, PdLβ_2, PKα_1, PKβ_1) and of binding energy values for Pd3d$_{5/2}$ and P2p$_{3/2}$ shows that (Fig. 2) in the complex the P → Pd bonding level contains large contribution of Pd4d function*.

It should be noted that the observed change of the a$_1$ level wavefunction of a free ligand L due to transition to Pd–P bonding level of a complex completely corresponds qualitatively to the change of the 5a$_1$ level in PH$_3$ due to transition to 7a$_1$ level in OPH$_3$, *viz.* according to calculations [11] this transition results in the sharp drop of the P3p orbital contribution (from 71 to 20 per cent) while the contribution of O2p orbital increases (Table III). This parallel is not accidental since both oxidation and coordination of PR$_3$ involve the conversion of the P atom's lone electron pair into the level of P–O or P–Pd σ-bond. Hillier *et al.* [12] mentioned this parallel however based on the change of the energy of a$_1$-type level in PF$_3$ at the transition to OPF$_3$ and to Ni(PF$_3$)$_4$ type complexes. It should be noted also that the A maximum of PKβ_1 line of PR$_3$ (R is alkyl) is normally more intensive than the B one in agreement with the calculations [11] for PH$_3$ and P(CH$_3$)$_3$. However if R = Ph the lone electron pair of P atom is partially delocalized due to interaction with the π-system of phenyl and in this case the A maximum is lower than the B one [10].

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*PdLβ_2 line is a superposition of transitions from molecular orbitals to Pd2p$_{3/2}$ level with relative intensities of transition being proportional to the Pd4d orbital contribution to the corresponding molecular orbitals.